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GB 2295271 A GB 0809644 A WO 99/03141 A1
US 5959329 A US 4505028 A

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(54) Abstract Title
Forming oxide layers in semiconductor layers

(57) A method of oxidising a layer of a semi conductor device comprises placing the device 14 in a furnace 10 and supplying a carrier gas such as nitrogen containing an oxidising vapour such as water vapour to the furnace. The device may be a VCSEL having an AlGaAs layer which is to be oxidised to form an optical aperture. The partial pressure of the water vapour is controlled by controlling the temperature of a water bath 18.

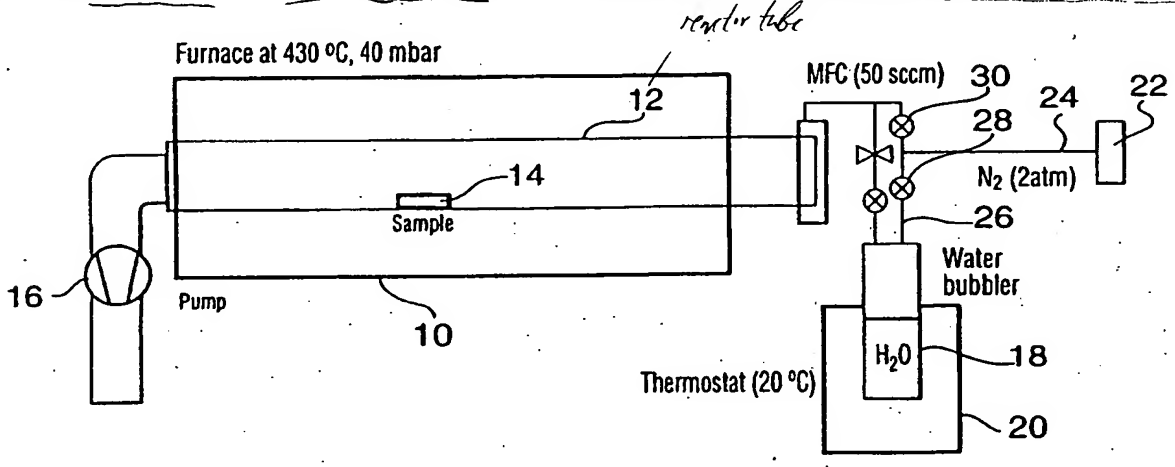

FIG. 1

GB 2 355 850 A

At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

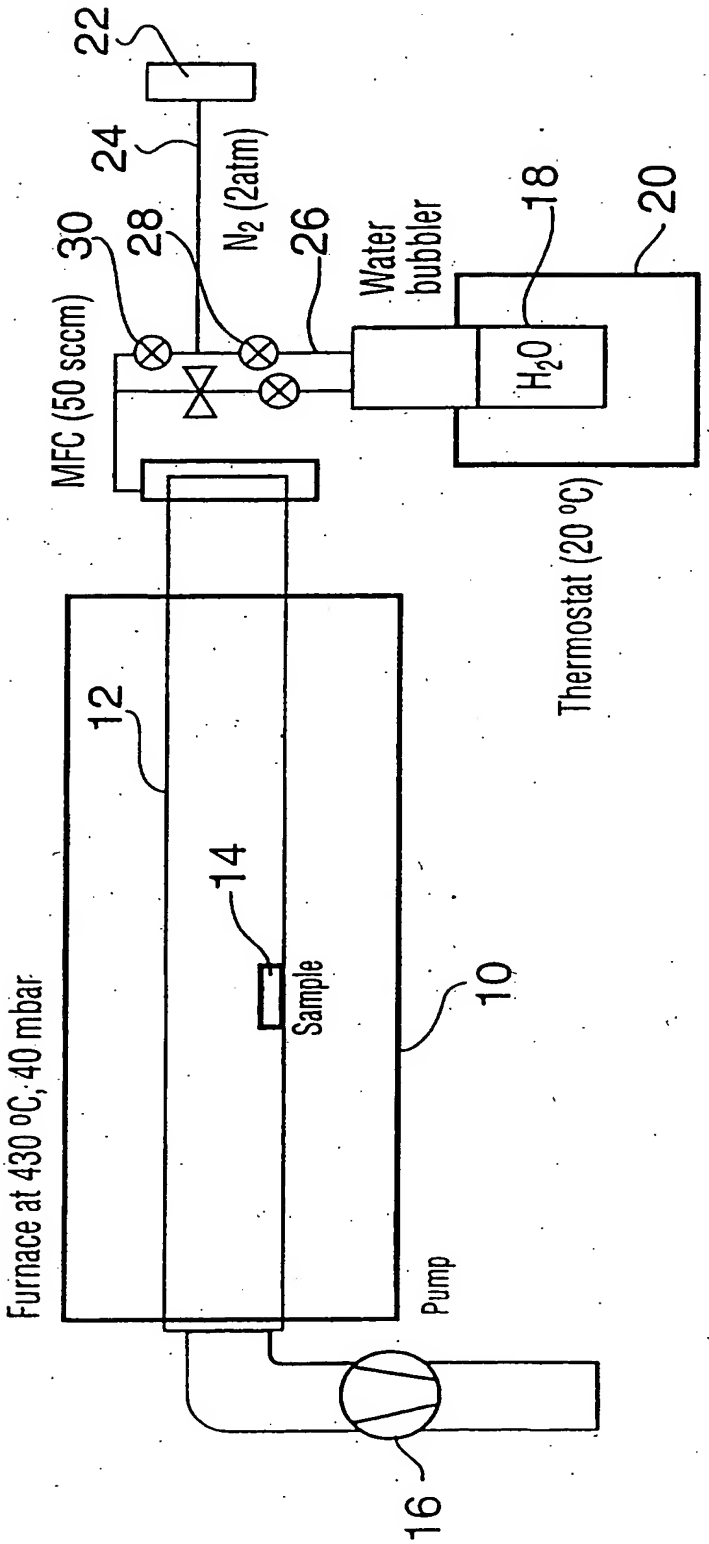
22
24
N_2 (2atm)
30
28
26
Water bubbler
18
20
MFC (50 sccm)
H_2O
Thermostat (20 °C)
12
14
Sample
10
Furnace at 430 °C, 40 mbar
Pump
16

FIG. 1

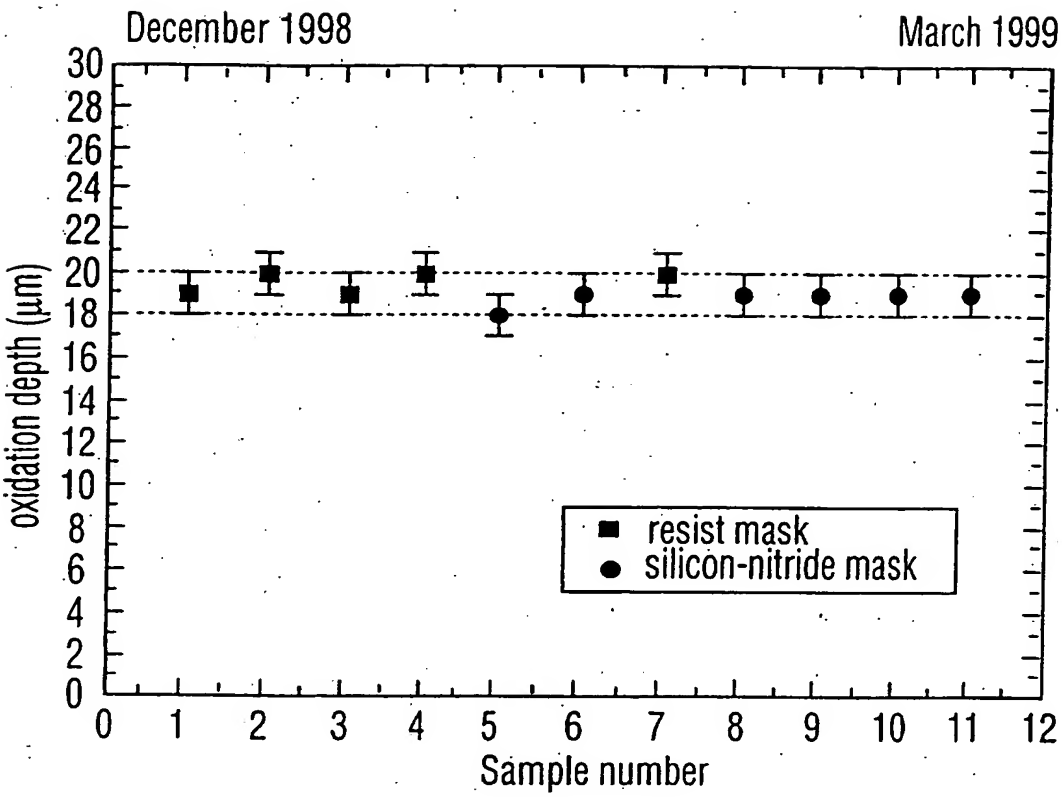
December 1998
March 1999
oxidation depth (µm)
Sample number
resist mask
silicon-nitride mask
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
0
1
2
3
4
5
6
7
8
9
10
11
12

FIG. 2

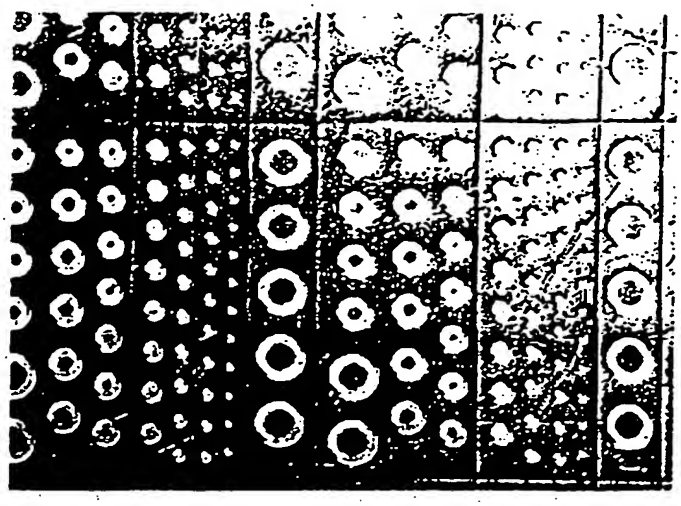

FIG. 3

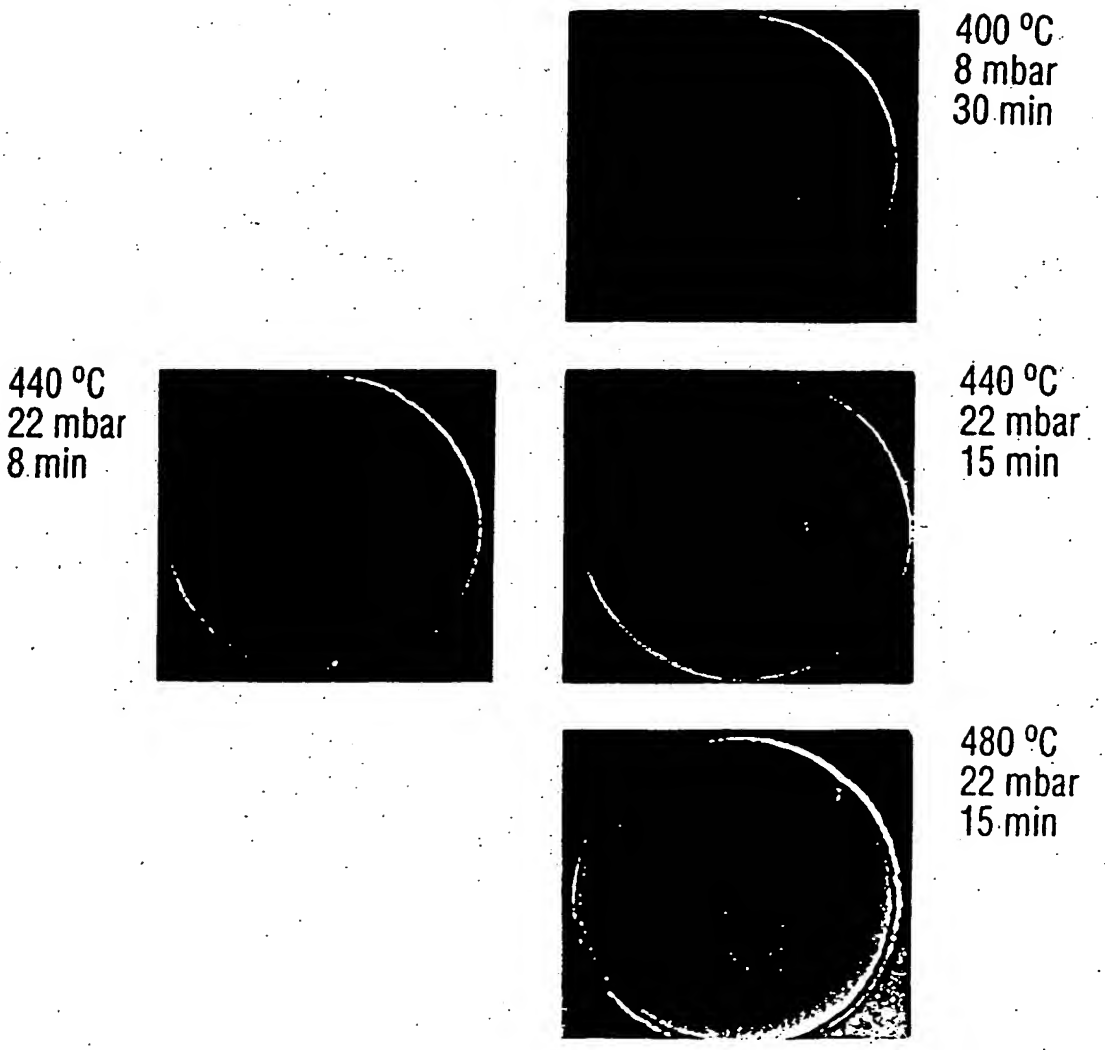
400 °C
8 mbar
30 min
440 °C
22 mbar
8 min
440 °C
22 mbar
15 min
480 °C
22 mbar
15 min

FIG. 4

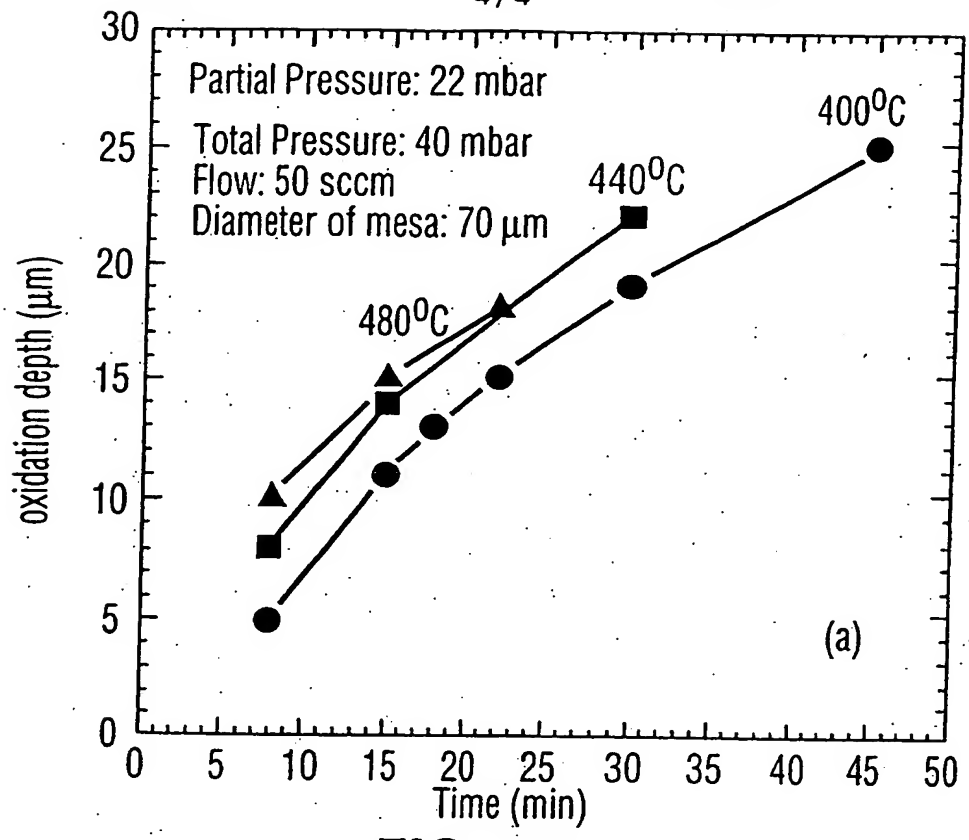
Partial Pressure: 22 mbar
Total Pressure: 40 mbar
Flow: 50 sccm
Diameter of mesa: 70 µm
400°C
440°C
480°C
(a)
oxidation depth (µm)
Time (min)
0
5
10
15
20
25
30
35
40
45
50

FIG. 5a

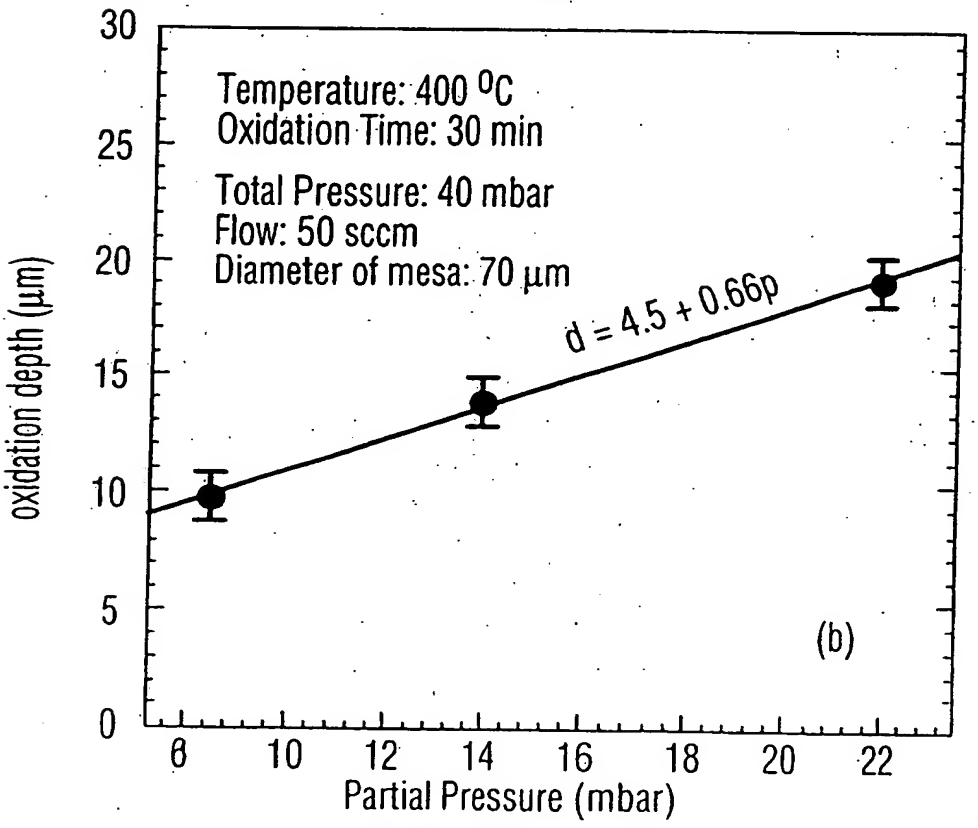
Temperature: 400 °C
Oxidation Time: 30 min
Total Pressure: 40 mbar
Flow: 50 sccm
Diameter of mesa: 70 µm
d = 4.5 + 0.66p
(b)
oxidation depth (µm)
Partial Pressure (mbar)
0
5
10
15
20
25
30
8
10
12
14
16
18
20
22

FIG. 5b

METHOD AND APPARATUS FOR THE CONTROLLED OXIDIATION OF MATERIALS

This invention relates to a method and apparatus for the controlled oxidation of materials, such as Al(Ga)As alloys.

In the optoelectronics industry, for example in the manufacture of LEDs and VCSELs (Vertical Cavity Surface Emitting Lasers), there is a need to effect the controlled conversion of Al(Ga)As to AlO_x in order to fabricate current or optical apertures. The oxidation process for converting Al(Ga)As to AlO_x is dependent on the kinetics of the oxidation reaction, supply of reactant (oxygen containing species) and removal of the by-products of the conversion reaction (e.g As). Unfortunately, this makes the Al(Ga)As-:>AlO_x conversion process very sensitive to factors such as temperature of the sample, composition of the Al(Ga)As material, the thickness of the layer, surface treatment prior to oxidation, amount of moisture in the reactive atmosphere of the furnace, exposure to air prior to the oxidation process, and opening/closing mode of the furnace when the sample is loaded. While some of these factors, such as temperature, can be relatively easily, others are very difficult if not impossible to control accurately enough (e.g. exposure to air, loading mode) and are generally considered "noise factors'". The many investigations on various Al(Ga)As oxidation processes that have been carried out by different researchers indicate a large variability in the process, suggesting a large contribution by the noise factors. This makes it difficult to control the conversion process with sufficient precision, resulting in a degradation of the device performance and an inability to produce higher speed devices.

An object of the invention is to alleviate this disadvantage.

According to the present invention there is provided a method of carrying out the controlled oxidation of an oxidisable material, comprising the steps of placing the oxidisable material into a reactor, and causing a carrier gas to flow over said oxidisable material, said carrier gas containing an oxidising vapour at a controlled partial pressure.

The oxidising vapour is typically water vapour and the carrier gas, and inert gas, typically nitrogen, in which case the partial pressure of the water vapour can be controlled by

controlling the temperature of a water bath, in turn to accurately control the oxidation process.

The oxidation process is typically carried out in a reactor tube at temperatures in the range of 400-500°C and pressures in the range of 50-100 mbar. These ranges are typical and not limiting. Precise control of the oxidation rate and of the final oxide thickness is achieved by controlling the partial pressure of the water vapor in the furnace tube.

The invention can be applied, for example, to the oxidation of Al(Ga)As in the manufacture of high speed VCSELs.

The process in accordance with the invention reduces the noise factors present when Al(Ga)As is converted AlO_x. The oxidation process is designed so that rate depends mainly on one control factor, namely the partial pressure of the oxidising vapour or the time of exposure.

The time of exposure can be controlled in practice by removing the sample from the oven or just turning off the water vapour.

Using the method of the invention, it has surprisingly been found that the reaction parameters can be chosen so that the oxidation process is tolerant to variations in temperature and total pressure in the furnace, to variations in the composition and thickness of the Al-containing layers or to the preparation of the samples.

While primarily intended for Al-containing layers, such as Al(Ga)As, the invention can be applied to other materials that need to be oxidised in a highly controlled manner.

Typically, the reaction is carried out at a low pressure, for example, 50-100mbar at temperatures in the range 400-500°C. These parameters are purely exemplary and not limiting. Persons skilled in the art can determine the optimum parameters for any particular application by routing experiment.

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The invention also provides an apparatus for carrying out the controlled oxidation of an oxidisable material, comprising a reactor for containing the oxidisable material, a supply of carrier gas for flowing over said oxidisable material, and a supply of oxidising vapour,

and a mixing device for mixing said oxidising vapour with carrier gas at a controlled partial pressure.

The apparatus and process parameters presented here provide for the precisely controlled oxidation of layered semiconductor structures including at least one layer of Al containing alloy. As a particular case, an isotropic oxidation rate can achieved for an AlAs alloy without addition of Ga.

The invention will now be described in more detail, by way of example only, with reference to the accompanying drawings, in which:-

Figure 1 shows an apparatus for carrying out the invention;

Figure 2 shows the reproducibility of the oxidation depth for various samples oxidised in accordance with the principles of the invention over a span of three months;

Figure 3 shows the uniformity of oxidation depth for mesas with various diameters and at different locations over the chip;

Figure 4 shows typical aspects of the oxide aperture; and

Figure 5a shows the dependence of oxidation depth on time for various furnace temperatures, and Figure 5b shows the dependence of the oxidation depth on partial pressure of water vapors for a temperature of the furnace of 400°C and a time of 30 minutes.

An apparatus for carrying out the novel method is shown in Figure 1. A furnace 10 with reactor tube 12 contains a sample to be oxidised, for example, a VCSEL precursor having an Al(Ga)As layer, which needs to be oxidised to form an optical aperture.

The furnace 10 heats the reactor tube to a temperature of 430°C and pump 16 evacuates it to a pressure of 40mbar.

A water bath 18 is heated to a temperature of 20°C by thermostatically controlled heater 20 to produce a controlled supply of water vapour. A source 22 supplies nitrogen at two atmospheres to supply line 24 where it is mixed with water vapour flowing along line 26 from the water bath 18. Valves 28 and 30 enable the flow rate of the water vapour and combined gases to be controlled. In this example, the flow rate is 50sccm.

The partial pressure of the water vapor is controlled by controlling the temperature of the water bath 18. The temperature of the reservoir is typically set in the range of 0-20°C, but it is not limited to this.

The design of the apparatus ensures that the partial pressure of the water vapor in the furnace is accurately maintained at the desired value and that it can be changed in a short time from zero to the desired working value ("on") and also from this value to a much lower, near-zero value ("off").

The oxidation time is accurately set by switching "on" and "off" the water vapor as the oxidation rate is negligible in the "off" state. The parameters are chosen such that the oxidation process is tolerant to variations in temperature and total pressure in the furnace, to variations in the composition and thickness of the Al- containing layers or to the preparation of the samples. Good reproducibility of the oxide thickness has been achieved with various samples over a time span of several months.

It will thus be seen in accordance with the principles of the invention that the reaction rate is directly controlled by the partial pressure of the water vapor fed into the reactor (furnace tube). The partial pressure of the water vapor is accurately set and maintained through the temperature of a water bath. This control is facilitated by having the reservoir in a thermostat bath at a near ambient temperature.

The design and construction of the water bath and of the lines feeding the gas mixture to the reactor provide for the accuracy of the control over the partial pressure of the water vapors in the reactor. The design relies on a fundamental physical law that states that at equilibrium the partial pressure of the water vapor is uniquely defined by the temperature of the vapor/liquid system to control the process.

The apparatus provides a means for effectively switching on and off the water vapor. When switched "on", the partial pressure of the vapor in the furnace tube will settle in a short time to the desired working value. When switched to "off" the partial pressure will be reduced to a near-zero value and only carrier gas only will flow through the furnace tube. This provides the way to define the oxidation time.

By conducting the reaction at a low pressure (50- 100 mbar range), good control can be ensures over residual gases enabling effective contaminant control.

The apparatus also has the advantage of low gas flows and easy-to-handle exhausts.

Figure 2 shows a series of samples taken over a period of three months. The square points are for a resist mask and the round points are for a silicon nitride mask. It will be seen that between December 1998 and March 1999, it was possible to maintain the oxidation depth between 18 and 20 μm.

Figure 3 illustrates the uniformity of oxidation depth for mesas with various diameters and different locations over the chip. This represents a significant improvement.

Figure 4 illustrates how both circular and rectangular windows can be formed with the invention. The circular shape results from an isotropic rate wherein the oxidation front copies the shape of the mesa, and the rectangular shape results from an anisotropic oxidation rate. The conditions for the various samples shown in Figure 4 were: 440°C at a partial pressure of 22mbar for 8 mins., 400°C at a partial pressure of 8mbar for 30 mins., 440°C at a partial pressure of 22 mbar for 15 mins., and 480°C at a partial pressure of 22 mbar for 15 mins.

Figures 5a shows the dependence of oxidation depth on time for various furnace temperatures. Figure 5b shows the dependence of the oxidation depth on the partial pressure of water vapour for a furnace temperature of 400°C and an exposure time of 30 mins.

In all cases, the oxidation depth is determined almost solely by the partial pressure of the water vapour and the exposure time. Unlike the prior art, in accordance with the principles of the invention the variables can be selected so that the noise parameters have very little impact on the oxidation process.

In summary, the process according to the principles of the invention offers easily controllable process parameters and oxidation time, very good reproducibility and stability, good uniformity, an isotropic rate without using ternary alloys, and is tolerant to sample preparation.

Although water vapour has been described as the oxidising vapour, the invention could also work with other oxidising vapours.

Claims:

1. A method of carrying out the controlled oxidation of an oxidisable material, comprising the steps of placing the oxidisable material in a reactor, and causing a carrier gas to flow over said oxidisable material, said carrier gas containing an oxidising vapour at a controlled partial pressure.

2. A method as claimed in claim 1, wherein the flow of said oxidising vapour is cut off after a predetermined time while maintaining flow of said carrier gas.

3. A method as claimed in claim 1 or 2, wherein said carrier gas is nitrogen.

4. A method as claimed in any one of claims 1 to 3, wherein said oxidising vapour is water.

5. A method as claimed in any one of claims 1 to 4, wherein said oxidising vapour is generated in a thermostatically controlled bath.

6. A method as claimed in claim 5, wherein the temperature of said bath is controlled to control the partial pressure of said oxidising vapour and thus the oxidation process.

7. A method as claimed in any one of claims 1 to 5, wherein said reactor is provided inside a furnace maintained a target temperature.

8. A method as claimed in claim 7, wherein said target temperature is about 400-500°C.

9. A method as claimed in any one of claims 1 to 8, wherein said reactor is maintained at a pressure of about 50-100mbar.

10. A method as claimed in any one of claims 1 to 9, wherein said material is an Al-containing layer.

11. A method as claimed in claim 10, wherein said material is Al(Ga)As.

12. A method as claimed in any one of claims 1 to 10 used in the manufacture of a VCSEL or LED.

13. An apparatus for carrying out the controlled oxidation of an oxidisable material, comprising a reactor for containing the oxidisable material, a supply of carrier gas for

flowing over said oxidisable material, and a supply of oxidising vapour, and a mixing device for mixing said oxidising vapour with carrier gas at a controlled partial pressure.

14. An apparatus as claimed in claim 13, comprising a thermostatically controlled bath for providing said oxidising vapour.

15. An apparatus as claimed in claim 13, wherein said thermostatically controlled bath is a water bath.

16. An apparatus as claimed in any one of claims 13 to 15, wherein said reactor is mounted in a furnace for maintaining said reactor at a high temperature.

17. An apparatus as claimed in any one of claims 13 to 16, further comprising a vacuum pump for maintaining a low pressure in said reactor.

18. An apparatus as claimed in any one of claims 13 to 17, further comprising mixing valves for controlling the relative flow rates of the oxidising vapour and the carrier gas.

Application No: GB 9925176.1 **Examiner:** COLIN STONE
Claims searched: All **Date of search:** 31 January 2000

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.R): H1K(KJACX)

Int Cl (Ed.7): H01L

Other: ON LINE,W.P.I.,EPODOC,JAPIO

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
X	GB 2295271 A	E.T.R.I. (See page 3 lines 14-17)	1,13
X	GB 0809644	WESTERN ELECTRIC (See page 4 lines 41-93)	1,13
X	WO 99/03141 A1	APPLIED MATERIALS (See page 9 lines 14-16)	1,13
X	US 5959329	TOSHIBA (See col.10 lines 23-56)	1,13
X	US 4505028	HITACHI (See col.4 lines 43-55)	1,13

X Document indicating lack of novelty or inventive step
Y Document indicating lack of inventive step if combined with one or more other documents of same category.
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